## COMPLETE SPECIFICATION

## Preparation of Zeolites X and Y

We, SOCONY MOBIL OIL COMPANY, INC., a company organised under the laws of the State of New York, United States of America, of 150 East 42nd Street, New York 17, New
5 York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following
10 statement:—

This invention relates to a method for converting natural clays to crystalline aluminosilicate zeolites. The word "crystalline" is used herein to include both wholly
15 crystalline and only partially crystalline. More particularly, the present invention is directed to a method for synthesizing crystalline aluminosilicate zeolites by treatment of natural clay with caustic-containing solutions
20 under particularly controlled and specified conditions. The invention also concerns a catalyst prepared by the method and a method of converting hydrocarbons employing the crystalline aluminosilicate of the invention.

25 In another embodiment, the invention is directed to a process for cracking heavy petroleum fractions to lighter materials boiling in the gasoline range in the presence of the aforesaid catalyst.

30 Of the presently commercially available cracking catalysts, a synthetic silica-alumina gel composite is by far the most widely used. While such type catalyst is superior in many ways to the earlier employed clay catalysts
35 and is fairly satisfactory, it is subject to improvement particularly in regard to its ability to afford a high yield of useful product with a concomitant small yield of undesired product.

40 During catalytic conversion of high boiling hydrocarbons to lower boiling hydrocarbons the reaction which takes place is essentially a cracking to produce lighter hydrocarbons but is accompanied by a number of complex side
45 reactions such as aromatization, polymeriza-

tion, alkylation and the like. As a result of these complex reactions, a carbonaceous deposit commonly called "coke" is laid down on catalyst. The catalyst is then regenerated by burning the coke therefrom in a stream of 50 oxidizing gas and the catalyst, so regenerated, is returned to the conversion stage of the cycle.

The ability of a cracking catalyst to control and to direct the course of conversion is 55 referred to as selectivity. Thus, an exceedingly useful and widely sought characteristic in a cracking catalyst is high selectivity.

Another important property desirable in a cracking catalyst is steam stability, i.e. the 60 ability not to become deactivated in the presence of steam at an excessively high rate.

Crystalline aluminosilicate zeolites structurally consist basically of an open three-dimensional framework of $SiO_4$ and $AlO_4$ 65 tetrahedra. Such tetrahedra are cross-linked by the sharing of oxygen atoms, so that the ratio of oxygen atoms to the total of the aluminum and silicon atoms is equal to two. The negative electrovalence of tetrahedra con- 70 taining aluminum is balanced by the inclusion within the crystal of cations, such as alkali or alkaline earth metal ions.

Many zeolites possess a crystal structure having channels of molecular dimensions and 75 are called "molecular sieves." The molecular sieve material may be of the A type, X type, Y type or other well known form of molecular sieve. Thus, molecular sieves available commercially include the 13X and 10X types 80 which are sodium and sodium-calcium crystalline aluminosilicates, capable of adsorbing molecules who critical diameter is less than about 10 Angstrom units. Both X and Y type crystalline aluminosilicates have essentially 85 identical crystal structures. These zeolites each contain a total of 192 silicon plus aluminum tetrahedra per unit cell. They differ from each other in chemical composition. Type X aluminosilicate has been 90

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characterized as having a unit cell formula within the range $M_{0.9}[(AlO_2)_{48}(SiO_2)_{96}]$ to and

including $M_{\frac{x}{n}}[(AlO_2)_{77}(SiO_2)_{115}]$. where M

is a cation of valence n. Type Y aluminosilicate has a higher $SiO_2/Al_2O_3$ ratio than shown in the latter formula. The terms zeolites X and Y accordingly do not refer to specific chemical entities of fixed composition, but rather refer to a range of compositions of essentially identical crystal structure.

The process of the present invention is directed particularly to conversion of a natural clay to synthetic aluminosilicate zeolites of the X and Y type. It has heretofore been proposed to prepare synthetic crystalline zeolites by initially calcining a clay at an elevated temperature, such as 500 to 800°C., for an extended period of time and thereafter aging the calcined clay with caustic at ambient temperatures for 2 to 3 days and finally reacting the aged mixture at a temperature approximating 100°C. for an additional period of time. Such three-step process, while affording conversion of the clay to synthetic zeolite, has proved to be time consuming and unattractive from a commercial standpoint.

In accordance with the present invention there is provided a new and improved method for converting natural clays to crystalline aluminosilicate zeolites. The method described herein has the very distinct advantage over previously suggested processes in that aging of the calcined clay with caustic at ambient temperatures over an extended period of time is eliminated and there is provided a much more rapid conversion of the clay to the desired crystalline zeolite product as compared with previously known processes.

In one embodiment, the present invention affords a method for preparing a hydrocarbon conversion catalyst by dispersing in a suitable matrix a finely divided product resulting from treatment of a natural clay as indicated hereinafter and drying and calcining the rustling composite.

In still another embodiment, the present invention affords a method for preparing a cracking catalyst having exceptional activity and selectivity consisting essentially of 2 to 90% by weight of a product having a weight mean particle diameter of less than 40 microns suspended in and distributed throughout a hydrous oxide matrix selected from the group consisting of clays and inorganic oxide gels, which product has been obtained by the process of the invention.

A particular example of the invention is a catalytic composition comprising spheroidal particles consisting essentially of 2 to 50 per cent by weight of a product having a weight mean particle diameter of between about 2 and about 7 microns suspended in and distributed throughout a matrix of an inorganic

oxide gel selected from the group consisting of alumina, silica and composites of silica with an oxide of at least one metal selected from the group consisting of metals of Groups IIA, IIIB, and IVA of the Periodic Table, which product has been obtained by the process of the invention.

The invention also includes a process for catalytic cracking of hydrocarbon oils in the presence of the above catalysts in accordance with which enhanced conversion of the charge stock to useful products is realized.

It has been found by maintaining certain critical composition limits within the reaction mixture that a clay upon contact with caustic and silica at a temperature between about 230°F. and about 1600°F. for a period of between about 3 minutes and about 72 hours and subsequent digestion of the resulting fused product in water at a temperature in the approximate range of 180°F. to 220°F. until crystalline aluminosilicate forms, usually for a period of at least about 8 and generally at least about 16 hours directly affords a high yield of crystalline aluminosilicate zeolite of the X—Y type. Naturally occurring hydrous aluminum silicate clays may be converted by the present process to crystalline molecular sieve type aluminosilicates. Clays undergoing conversion in accordance with the present method generally contain at least one of the following as the chief mineral constituent: kaolinite, halloysite, montmorillonite, anauxite, nacrite and dickite. While clays of the foregoing type generally may be treated in the process of this invention including those which have undergone previous acid treatement and/or calcination, it is a preferred embodiment to employ directly a raw uncalcined natural clay, thereby further speeding up the conversion process with elimination of the initial clay calcination step, essential in the previously known processes.

The first step of the present process comprises treating the clay in the form of an aqueous slurry with an alkali metal hydroxide, preferably sodium hydroxide, having reactable silica added thereto, under conditions of substantially atmospheric pressure and at a temperature above about 230°F. and preferably above about 400°F. but not exceeding about 1600°F. The duration of such treatment will depend largely on the temperature employed and may extend from about 3 minutes at a temperature of 1600°F. to about 72 hours at a temperature of about 230°F. Preferably, a reaction period of between about 3 minutes and about 5 hours at a temperature in the aproximate range of 400°F. to 1600°F. is employed. Utilizing a reaction temperature of 1000—1200°F., the period of treatment is approximately one half hour. Under the foregoing conditions, a fused aluminosilicate composite or frit, is formed.

In the second step of the process, the fused

material or frit is dispersed in water, preferably after being ground to a finely divided state of generally less than 60 mesh. Digestion of the dispersed solid in the resulting aqueous alkaline solution maintained at a temperature within the approximate range of 180°F. to 220°F. is carried out for a period of at least about 8 and preferably greater than 16 hours. Generally, the digestion period does not exceed about 72 hours, although longer periods may be used without adverse effect on the resulting crystalline aluminosilicate product.

To achieve a resulting aluminosilicate of high crystallinity, it has been found desirable to disperse the finely ground solid in the water in a closely controlled manner prior to the digestion step. Initially, the finely ground solid is slurried at a fairly high concentration, utilizing a water to solid weight ratio of approximately 1 to 3 for a short interval of time, generally not exceeding about 30 minutes. Thereafter, the slurry is diluted with a large volume of water bringing the molar ratio of water to total alkali metal oxide within the approximate range of 35 to 180, after which digestion proceeds as described above. The resulting highly adsorbent crystalline sodium aluminosilicate product is removed from the reaction mixture, suitably washed free of soluble matter and thereafter dried. X-ray analysis of the product so obtained shows the same to be a crystalline aluminosilicate of the X—Y type.

The slurry of aluminosilicate resulting from treatment of natural clay, as described above, may suitably be formed into very finely divided particles by spray drying. The product so obtained being made up of particles having a diameter of less than 300 microns. Such product is particularly applicable for use in operations employing a fluidized particle-form contact material. It is, in fact, one of the advantages of the present invention that the treatment of natural clay with a caustic-containing solution may be controlled to afford a product of predetermined crystallinity and the slurry resulting from such controlled treatment thereafter be formed into particles of desired size by various techniques, such as spray drying. The slurry of aluminosilicate may be dispersed in the upper part of a chamber or tower through which a current of drying gas is passed. The drying gas, which may be air, is usually supplied in heated conditions generally at a temperature between about 600°F. and 1000°F. to accelerate the rate of drying of the particles. Dispersion may be effected by any well known method such as impinging a stream thereof on to a rapidly rotating disc by forcing it through a nozzle provided with multiple orifices or by spraying through a nozzle designed to impart a high velocity to the slurry and break up into fine particles of relatively uniform size. Contact between the hot gases and the product is maintained for a relatively short interval of time. The slurry prior to spraying usually contains between about 4 and about 10 per cent solids. It is generally preferred to disperse the slurry in the form of droplets having a diameter of about 200—400 microns which, on drying, results in a product of about 100—300 microns diameter.

Ratios of total alkali metal oxide/water-free clay, silica/water-free clay and water/total alkali metal oxide, as well as the temperature and time of contact during the initial high temperature step and the subsequent digestion step should be precisely controlled. Products which vary from primarily amorphous (low crystallinity) to those which possess a high degree of crystallinity are prepared by controlling the total alkali metal oxide/water-free clay weight ratio within the range of 0.95 to 7.4 and added $SiO_2$/water-free clay weight ratio within the range of 0.01 to 3.8. Products having more than 50 per cent crystallinity corresponding to high adsorptive properties are prepared by controlling the total alkali metal oxide/water-free clay weight ratio within the range of 1.1 to 6.6 and added $SiO_2$/water-free clay weight ratio within the range of 0.01 to 3.7. Silica or a compound capable of furnishing silica under the reaction conditions must be present in the initial high temperature reaction mixture to afford a product possessing a high degree of crystallinity. Such silica may be added from any suitable source such as alkali metal silicate, sand, quartz, siliceous earths, colloidal silica, silica gel and ethyl ortho silicate.

The reaction conditions and concentrations of reactants employed in the present method may be summarized as follows:

| Reaction Conditions | Limits for low crystallinity | Limits for 50% crystallinity | Limits for High crystallinity |
|---|---|---|---|
| Wt. Ratio total alkali metal oxide/water-free clay | 0.95 – 7.4 | 1.1 – 6.6 | 1.1 – 5.1 |
| Wt. Ratio added $SiO_2$/water-free clay | 0.01 – 3.8 | .01 – 3.7 | 0.19 – 3.3 |
| Mole Ratio $H_2O$/total alkali metal oxide | 35 – 180 | 35 – 180 | 35 – 115 |

The degree of clay conversion can be controlled by the variables above indicated. Materials ranging from low to highly crystalline alkali metal aluminosilicate may be prepared. Products having a high degree of adsorption as measured by the ability to adsorb above about 11 per cent by weight of cyclohexane are characterized by X-ray analysis as having a major proportion of crystalline aluminosilicate of the 13X type with some shift, generally 10 to 40 per cent, to the 13Y structure. The materials having high cyclohexane adsorption were found, upon analysis, to be substantially entirely X—Y type crystalline aluminosilicates. Thus, due to the simplicity of the cyclohexane adsorption test, this parameter was used herein to characterize present products. The relationship between crystallinity, by X-ray analysis, and cyclohexane adsorption is shown graphically in Figure 1.

The products obtained, as indicated hereinabove, are crystalline alkali metal aluminosilicate molecular sieve zeolites. Other ions may, if desired, be introduced into the zeolite structure by base exchange of the alkali metal ions. Such exchange cation replaces the alkali metal ions and modifies the adsorption and catalytic properties of the zeolite. Suitable replacing ions include monovalent or divalent cations, such as silver and magnesium; calcium or strontium; metal ions of the transition metals; the rare earth metals (i.e. the elements having atomic numbers 57—71 inclusive plus scandium and yttrium; alkaline earth metal ions and other ions, for example, hydrogen ions and ammonium which can behave as metals in replacing alkali metal ions without causing any appreciable change in the basic structure of the zeolite crystal. The transition metals are those whose atomic numbers are from 21 to 28, from 39 to 46 and from 72 to 78 inclusive, e.g. titanium, vanadium, manganese, iron, cobalt, nickel, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, platinum, hafnium, tantalum, tungsten, rhenium, osmium and iridium. It is also within the purview of the present invention to introduce the foregoing ions into the structure of the resulting crystalline aluminosilicate while retaining the aforementioned alkali metal oxide/clay ratio during the initial high temperature step by including in the reaction mixture a suitable compound of the metal which it is desired to so introduce. The resulting product is thereafter dispersed in water and subjected to the digestion treatment described hereinabove. The ions which are base-exchanged may reduce the alkali metal content of the treated aluminosilicate to below 3 per cent by weight.

The following Examples will serve to illustrate the method of this invention, except for Examples 5, 6 and 17—19 which are for comparative purposes:

## EXAMPLE 1

Dixie clay used in this preparation is a kaolinite having the following composition: 44.51 wt.% $Al_2O_3$, 38.51 wt.% $SiO_2$, 1.27 wt.% $Fe_2O_3$, 1.47 wt.% $TiO_2$, 0.08 wt.% $CaO$, 0.12 wt.% $MgO$, 0.08 wt.% $Na_2O$, 0.22 wt.% $K_2O$, 13.41 wt.% loss at 1100°F.

Fifty (50) grams of the above clay were mixed in a blendor with 100 grams NaOH containing 77.5 wt.% $Na_2O$, 50 cc of water and 92 grams N-Brand sodium silicate containing 8.8 wt.% $Na_2O$, 28.5 wt.% $SiO_2$, and 62.7 wt.% $H_2O$. The resulting wet slurry was placed in a furnace at 600°F, and held for four hours permitting the temperature of the slurry to increase from room temperature to 600°F.

The product which formed was a hard crusty solid. This material was ground to a particle size of less than 60 mesh (Tyler). The ground material was then contacted with water using 1 gram of water per gram of solid for about 2 minutes while being vigorously agitated in a blendor. To the resulting slurry was added 1890 cc of water. The mixture so obtained was agitated for at least about 2 minutes and thereafter contacted for 44 hours at 200°F. in a static state.

The resulting product which settled to the bottom of the digestion vessel was separated from supernatant liquid by decanting, and thereafter filtered and washed. The wet cake so obtained was dried in air at 230°F.

Cyclohexane adsorption data for this product showed 17.3 weight per cent adsorption illustrating the same high degree of adsorption characterizing the crystalline sodium aluminosilicate of the X-type. X-ray analysis further showed that the product was about 85% 13X type sodium aluminosilicate having approximately a 15% shift in parameter to the 13Y type aluminosilicate.

## EXAMPLES 2—5

The products of these examples were made in the same manner as in Example 1 except that the total caustic to clay weight ratio was varied. Thus, in Example 1, such ratio was 1.71 grams $Na_2O$ per gram of water-free clay. In Example 2 and 3, the total caustic to water-free clay weight ratio was 1.95 and 2.18 grams $Na_2O$ per gram of clay, respectively. In Examples 4 and 5, the total caustic to water-free clay weight ratio was reduced to 1.33 and 0.94 grams $Na_2O$ per gram of clay, respectively. The data for these examples together with cyclohexane adsorption data for each product are hereinafter summarized in Table I. As will be seen from such data at the silica to clay weight ratio employed (0.525 gram silica/gram of water-free clay), appreciable deviation of the total caustic to clay weight ratio from that employed in Example 1 resulted in products having a lower adsorption capacity for cyclohexane.

## EXAMPLE 6

The product of this example was made in essentially the same manner as in Example 1, but the caustic and silicate were decreased, the $Na_2O$ to clay weight ratio being 0.856 and the $SiO_2$ to clay weight ratio being 0.262. The details of preparation and the cyclohexane adsorption data for this product are hereinafter shown in Table I.

## EXAMPLE 7

The product of this example was made in essentially the same manner as in Example 1, but the silica/clay weight ratio was increased to 1.05 grams $SiO_2$/gram clay. The preparation and cyclohexane adsorption data for this product are hereinafter shown in Table I and indicate that at higher levels of caustic to clay, the silicate to clay weight ratio also has to be increased to maintain a product of high crystallinity.

## EXAMPLE 8

The product of this example was made in essentially the same manner as in Example 1, but with a higher $Na_2O$/clay weight ratio of 3.64 and with a higher $SiO_2$/clay weight ratio of 0.855. As will be seen from the cyclohexane adsorption data obtained and summarized in Table I below, a satisfactory crystalline product was produced.

TABLE I

| Example No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| **Fusion Composition** | | | | | | | | |
| Clay Type | Raw Dixie Clay → | | | | | | | |
| Wt., g. | 50 → | | | | | | | |
| Caustic NaOH, g. | 100 | 115 | 130 | 75 | 50 | 50 | 130 | 219 |
| Silicate (1) N-Brand, g. | 92 | — | — | — | — | 46 | 184 | 150 |
| Water g | 50 → | | | | | | | |
| g. $Na_2O$(total)/g. clay | 1.72 | 1.95 | 2 18 | 1.33 | 0.94 | 0.856 | 2.35 | 3.64 |
| g. Added $SiO_2$/g. clay | 0.525 | — | — | — | → | 0.262 | 1.05 | 0.855 |
| Total Moles $Na_2O$(3) | 1.83 | 2.08 | 2.33 | 1.42 | 1.00 | 1.28 | 1.58 | 2.86 |
| Total Moles $SiO_2$ | | | | | | | | |
| **Conditions** | | | | | | | | |
| Time, Hrs. | 4 → | | | | | | | |
| Temp., °F. | 600 | — | — | — | → | 1000 | 600 | 600 |
| **Predigestion** | | | | | | | | |
| Volume $H_2O$, ml. | 125 → | | | | | | | |
| Time, Min. | 2 → | | | | | | | |
| **Digestion** | | | | | | | | |
| Volume $H_2O$, ml. | 1890 → | | | | | | | |
| Time, Hrs. | 44 → | | | | | | | |
| Temp., °F. | 200 → | | | | | | | |
| Cyclohexane Adsorption of Dried (2) Filter Cake Wt. % | 17.3 | 17.2 | 13.3 | 15 5 | 1.1 | 4.9 | 17.8 | 12.1 |

(1) 28.5% $SiO_2$, 8.8% $Na_2O$, 62.7% $H_2O$

(2) Cake dried 20 hours at 230° F.

(3) Mole ratio including $Na_2O$ in NaOH and N-Brand and $SiO_2$ from N-Brand and clay.

EXAMPLES 9—19

The products of these examples were prepared in the same manner as in Example 1 except that the caustic to clay and silica to clay ratios in the reaction mixture were varied. The details of preparation and the cyclo-hexane adsorption data for each of the resulting products are shown below in Table II:

## TABLE II

| Example No. | 9 | 10 | 3 | 11 | 7 | 12 | 13 | 14 | 4 | 15 | 16 | 17 | 6 | 18 | 19 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Fusion** | | | | | | | | | | | | | | | |
| Composition | | | | | | | | | | | | | | | |
| Clay | | | | | | | | | | | | | | | |
| Type | Raw Dixie Clay --------------------------------------------------→ | | | | | | | | | | | | | | |
| Wt., g. | 50 ----------------------------------------------------------→ | | | | | | | | | | | | | | |
| Caustic | | | | | | | | | | | | | | | |
| NaOH, g. | 130 | 130 | 130 | 130 | 130 | 75 ---------------------→ | | | | | | 50 ------→ | | 50 |
| Silicate (1) | | | | | | | | | | | | | | | |
| N-Brand, g. | 0 | 46 | 92 | 125 | 184 | 0 | 23 | 46 | 92 | 125 | 184 | 0 | 46 | 92 | 46 |
| Water, g. | 50 ----------------------------------------------------------→ | | | | | | | | | | | | | | |
| g.Na₂O(Total)/g. Clay | 2.02 | 2.10 | 2.18 | 2.24 | 2.34 | 1.16 | 1.21 | 1.25 | 1.33 | 1.39 | 1.49 | 0.77 | 0.856 | 0.935 | 0.856 |
| g.Added SiO₂/g. Clay | 0 | 0.262 | 0.525 | 0.712 | 1.05 | 0 | 0.13 | 0.262 | 0.525 | 0.712 | 1.05 | 0 | 0.262 | 0.524 | 0.262 |
| $\dfrac{\text{Total Moles Na}_2\text{O (3)}}{\text{Total Moles SiO}_2}$ | 5.07 | 3.16 | 2.33 | 1.98 | 1.57 | 2.93 | 2.26 | 1.88 | 1.41 | 1.23 | 1.00 | 1.95 | 1.28 | 1.00 | 1.28 |
| Conditions | | | | | | | | | | | | | | | |
| Time, Hrs. | 4 ------------------------------------------------→ 4 ------------→ 4 | | | | | | | | | | | | | | |
| Temp., °F. | 600 ------------------------------------------→ 1000 ----------→ 600 | | | | | | | | | | | | | | |
| Predigestion | | | | | | | | | | | | | | | |
| Volume H₂O, ml. | 125 ---------------------------------------------------------→ | | | | | | | | | | | | | | |
| Time, Min. | 2 -----------------------------------------------------------→ | | | | | | | | | | | | | | |
| Digestion | | | | | | | | | | | | | | | |
| Volume H₂O, ml. | 1890 --------------------------------------------------------→ | | | | | | | | | | | | | | |
| Time, Hrs. | 44 ----------------------------------------------------------→ | | | | | | | | | | | | | | |
| Temp., °F. | 200 ---------------------------------------------------------→ | | | | | | | | | | | | | | |
| Cyclohexane Adsorption | | | | | | | | | | | | | | | |
| Dried Filter Cake (2) Wt. % | 2.0 | 1.5 | 13.3 | 15.5 | 17.8 | 6.8 | 12.7 | 15.4 | 15.5 | 10.8 | 1.0 | 1.1 | 4.9 | 1.5 | 2.4 |

(1) 28.5% SiO₂, 8.8% Na₂O, 62.7% H₂O
(2) Cake dried 20 hours at 230° F.
(3) Mole ratio including Na₂O in NaOH and N-Brand and SiO₂ from N-Brand and clay.

The above summarized examples show the effect of the ratio of added silica to clay at fusion conditions for various caustic/clay levels. Thus, the products of Examples 9, 10, 3, 11 and 7 were prepared as in Example 1 except that the added caustic to clay weight ratio was held constant at 2.6 grams NaOH per gram of water-free clay, while the amount of added silica was increased from 0 to 0.262, 0.525, 0.712 and 1.05 gram/gram of water-free clay respectively. Silica was added as N-Brand sodium silicate containing 28.5 weight per cent. $SiO_2$ and 8.8 weight per cent $Na_2O$. Cyclohexane adsorption data on the finished products, show an increase from 2.0 and 1.5 for Examples 9 and 10 to 13.3, 15.5 and 17.8 for Example 3, 11 and 7, respectively. These data establish that the product quality can be controlled from 1.5 weight per cent to 17.8 weight per cent cyclohexane adsorption by controlling the added silica to clay weight ratio between 0.26 and 1.05 at a caustic ($Na_2O$) to clay weight ratio of 2.02/1.

Examples 12, 13, 14, 4, 15 and 16 demonstrate the effect of added N-Brand sodium silicate at a lower caustic to clay weight ratio of 1.5 grams NaOH/gram of clay. The added silica, as sodium silicate, was increased from 0 to 1.05 grams/gram of clay showing that at this caustic/clay weight ratio (1.16 grams $Na_2O$/gram of clay) suitable product, having an adsorption capacity for cyclohexane of 6.8 weight per cent, was prepared with no added silicate. These data summarized in Table II show optimum activation at a NaOH/clay weight ratio of 1.5 when between 0.2 and 0.6 gram silica (as silicate) was used per gram of clay.

Examples 17, 6 and 18 show the effect of increased silica utilizing a low caustic/clay weight ratio of 1 gram NaOH/gram of clay. The fusion temperature was increased for these examples to favor further reactivity of the components. Example 6 demonstrates that at the low caustic/clay weight ratio, the optimum silica to clay weight ratio is about 0.26 gram $SiO_2$/gram of clay. However, at these low levels of added caustic and silicate, the product quality, as measured by cyclohexane adsorption, was much lower, i.e. 4.9 weight per cent, as compared with 15.4 weight per cent when a caustic to clay weight ratio of 1.5 was employed.

The product of Example 19 was prepared in the same manner as Example 6 but at a temperature of 600°F. This lower temperature was insufficient to appreciably activate the clay with the low caustic to clay weight ratio utilized as evident from the lower adsorption of cyclohexane realized with the resulting product.

Examples 20, 21, 22, 23, 4, 24, 25, 26, 27, 28, 29, 30 and 31 show the effect of fusion temperature on product quality. The products of these examples were prepared in the same manner as in Example 1 except that the furnace temperature was varied over a range from 230°F. to 1600°F. The details of preparation and the cyclohexane adsorption data obtained with each of the products are shown below in Table III:

TABLE III

| Example No. | 20 | 4 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Fusion** | | | | | | | | | | | | |
| Composition | | | | | | | | | | | | |
| Clay | | | | | | | | | | | | |
|   Type | Raw Dixie Clay → | | | | | | | → | Raw McNamee Clay → | | | |
|   WT., g. | 50 | — | — | — | — | — | — | — | — | — | — | — |
| Caustic NAOH, g. | 75 | — | — | — | — | — | — | — | — | — | — | — |
| Silicate (1) N-Brand, g. | 92 | — | — | — | — | — | — | — | — | — | — | — |
| Water, g. | 50 | — | — | — | — | — | — | — | — | — | — | — |
| g. Na$_2$O(Total)/g. Clay | 1.33 | — | — | — | — | — | — | — | — | — | — | — |
| g. Added SiO$_2$/g. Clay | 0.524 | — | — | — | — | — | — | — | — | — | — | — |
| Total Moles Na$_2$O (3) | 1.42 | — | — | — | — | — | — | — | — | — | — | — |
| Total Moles SiO$_2$ | | | | | | | | | | | | |
| **Conditions** | | | | | | | | | | | | |
|   Time, Hrs. | 4 | — | — | — | — | — | — | — | → 24 | 1/2 | 72 | 72 |
|   Furnace Temp., °F. | 450 | 600 | 800 | 800 | 1000 | 1200 | 1400 | 1600 | 400 | 1000 | 230 | 350 |
| **Predigestion** | | | | | | | | | | | | |
|   Volume H$_2$O, ml. | 125 | — | — | — | — | — | — | — | — | — | — | — |
|   Time, Min | 2 | — | — | — | — | — | — | — | — | — | — | — |
| **Digestion** | | | | | | | | | | | | |
|   Volume H$_2$O, ml. | 1890 | — | — | — | — | — | — | — | — | — | — | — |
|   Time, Hrs. | 44 | — | — | — | — | — | — | — | — | — | — | — |
|   Temp., °F. | 200 | — | — | — | — | — | — | — | — | — | — | — |
| Cyclohexane Adsorption Dried Filter Cake (2) Wt % | 13.9 | 15.4 | 12.5 | 13.6 | 15.6 | 17.0 | 15.9 | 10.5 | 15.2 | 16.0 | 11.4 | 15 |

(1) 28.5% SiO$_2$, 8.8% Na$_2$O, 62.7% H$_2$O
(2) Cake dried 20 hours at 230° F.
(3) Mole ratio including Na$_2$O in NaOH and N-Brand and SiO$_2$ from N-Brand and clay.

The foregoing data show that the minimum temperature is 230°F. when fusing for 72 hours. The product quality determined by cyclohexane adsorption, as will be noted, is essentially constant over the broad range of fusion temperature of 450°F. to 1500°F. Higher temperatures of operation favor shorter contact times. At 1000°F., for example, a 1/2 hour contact (Example 28) gave comparable results to treatment at 600°F. for 4 hours (Example 4) or at 400°F. for 24 hours (Example 27). At 230 and 350°F., a 72 hour contact time was sufficient to yield desirable product.

In addition to Dixie clay, various other clays were treated utilizing the procedure of Example 1 including bentonite, halloysite and other kaolinites such as McNamee, Georgia and Florida clays by contacting in each instance a 50 gram sample of the clay with 100 grams NaOH (77.5 wt.% $Na_2O$), 92 grams of N-Brand sodium silicate and 50 cc of water. The resulting wet slurry was placed in a furnace at 600°F. and so maintained for 4 hours allowing the temperature of the slurry to increase from room temperature to 600°F. The product obtained in each instance was ground to less than 60 mesh (Tyler) and the finely ground material was contacted for 44 hours at 200°F. utilizing a dilution of 40.2 grams of water per gram of clay. The product so obtained, in each instance, was filtered, washed and dried in air at 230°F. Cyclohexane adsorption data were obtained for each of the products. The data summarized in Figure 2 show that the present method is broadly applicable to clays in general. The optimum activation conditions, as will be noted, was at approximately the same total caustic/clay weight ratio of 1.72 grams $Na_2O$ per gram of clay regardless of whether the clay was bentonite (montmorillonite), halloysite of the kaolinite type as Dixie, McNamee, Georgia or Florida clay.

The effect of total $Na_2O$ concentration in the digestion mixture is shown in Figure 3. Examples 31—36 from which such data were obtained were carried out in the same manner as Example 4 reacting 50 grams of clay with 75 grams NaOH and 92 grams N-Brand sodium silicate. These samples were digested at 200°F. for 21 hours at various dilutions from 14 moles $H_2O$/mole $Na_2O$ to 263 moles $H_2O$/mole $Na_2O$. These data show that the preferred dilution of the digestion mixture corresponds to about 35 to 180 moles $H_2O$/mole $Na_2O$ and more particularly to about 35 to about 115 moles $H_2O$/mole $Na_2O$ to yield crystalline material of 50 per cent or greater crystallinity as measured by X-ray analysis. Also included in Figure 3 are data from Example 37 for a crystalline material prepared in the same manner as Example 4 except that sand instead of sodium silicate was used as the source of silica. At the molar dilution of 120 moles of $H_2O$ per mole $Na_2O$, the product resulting from this preparation had a cyclohexane adsorption of 12.6, showing that sources of silica other than sodium silicate are feasible for use in the method of this invention.

The foregoing data establish limits on the binary ratios of reactants. Since such ratios are interdependent one upon the other, the actual composition of the initial reaction mixture employed in the present method is summarized in Figure 4. Such ternary diagram shows the limits in terms of the weight per cent of water-free clay, sodium oxide and added silica. Such were defined by the cyclohexane adsorption properties of the products obtained. The permissible composition limits are defined by the area ABCD of Figure 4. Such includes sodium aluminosilicate products having crystal patterns of the X and Y type and having cyclohexane adsorption above about 11 per cent and crystallinity above about 50 per cent. The preferred region of compositions for at least about 80 per cent crystallinity having a cyclohexane adsorption of at least about 16 weight per cent fall within the area defined as EFGH.

The following example serves to demonstrate that colloidal silica may be employed as the source of silica in the present process.

EXAMPLE 38

Fifty (50) grams of raw McNamee clay was mixed with 85.7 grams NaOH containing 77.5 wt.% $Na_2O$, 45.5 grams of water and 88.6 grams of a silica sol containing 30 weight per cent $SiO_2$, known commercially as Ludox. Mixing was carried out with vigorous agitation for about 2 minutes.

The resulting slurry was charged to a furnace at 600°F. and held at this temperature for 4 hours. The resulting fused product was crushed to a particle size of less than 60 mesh (Tyler) and mixed with 120 cc of water for 2 minutes. The pre-digested slurry was thereafter diluted with 1890 cc of water and digested in a covered container for 21 hours at 200°F.

The resulting product which settled to the bottom of the digestion vessel was separated from supernatant liquid by decanting, and thereafter filtered and washed free of excess caustic and silicate with water. The wet cake so obtained was then dried.

Cyclohexane adsorption data for this product showed 17.3 weight per cent adsorption illustrating the same high degree of adsorption characterizing the crystalline sodium aluminosilicate of the X-type and confirming the high degree of crystallinity.

The following example serves to illustrate that the process of the invention is applicable to calcined clay, affording results similar to those obtained with raw clay.

## EXAMPLE 39

Forty-three and three tenths (43.3) grams of McNamee clay previously calcined at 1450°F. for 2 hours was mixed with 75 grams NaOH containing 77.5 wt.% Na$_2$O, 50 grams of water and 92 grams N-Brand sodium silicate containing 8.8 wt.% Na$_2$O, 28.5 wt.% SiO$_2$ and 62.7 wt.% H$_2$O. The resulting wet slurry was charged to a furnace at 600°F. for 4 hours.

The product which formed was a hard crusty solid. This material was ground to a particle size of less than 60 mesh (Tyler) and mixed with 120 cc of water for 2 minutes. The pre-digested slurry was thereafter diluted with 1890 cc of additional water and digested in a covered container for 21 hours at 200°F.

The resulting product which settled to the bottom of the digestion vessel was separated from supernatant liquid by decanting and thereafter filtered and washed. The wet cake so obtained was dried in air at 230°F.

The product so obtained showed 14.7 weight per cent cyclohexane adsorption corresponding approximately to 70 per cent. crystallinity.

The base exchanged aluminosilicate product may be used directly as a catalyst for effecting conversion of hydrocarbons. Alternatively, the base exchanged aluminosilicate may be intimately admixed in finely divided form with a binder therefor under such conditions that the aluminosilicate is distributed throughout and held suspended in a matrix of the binder which may subsequently be dried and calcined. Thus, the catalyst utilized in the present process may, in one embodiment, be prepared by intimately admixing the alkali metal aluminosilicate prepared, as described hereinabove, in finely divided form having a weight mean particle diameter of less than about 40 microns and preferably less than about 15 microns with a suitable binder such as clay or an inorganic oxide gel, base exchanging the resulting composite substantially free of alkali metal by treating with a solution containing at least one ion selected from the group of alkaline earth metals, rare earth metals, ammonium and hydrogen, washing the resulting base exchanged material free of water soluble matter, drying the washed composite and subjecting the same to a thermal activating treatment. Alternatively, the alkali metal aluminosilicate may undergo base exchange, as above, prior to intimate admixture thereof with the binder. In accordance with such manner of operation, the resulting mixture of finely divided previously base exchanged aluminosilicate distributed throughout and held suspended in a matrix of the binder is dried and thermally activated as described hereinabove.

Intimate admixture of the finely divided base exchanged aluminosilicate and binder, such as inorganic oxide hydrogel, may be accomplished, for example, by ball milling the two materials together over an extended period of time preferably in the presence of water under conditions to reduce the particle size of the aluminosilicate to a weight mean particle diameter of less than 40 and preferably less than 15 microns. Such method of admixture, however, is less preferred than that achieved by dispersing the powdered aluminosilicate either before or after drying, in an inorganic oxide hydrosol. Following this procedure, the finely divided aluminosilicate may be dispersed in an already prepared hydrosol or, as is preferable where the hydrosol is characterized by a short time of gelation, the finely divided aluminosilicate may be added to one or more of the reactants used in forming the hydrosol or may be admixed in the form of a separate stream with streams of the hydrosol-forming reactants in a mixing nozzle or other means where the reactants are brought into intimate contact. It is desirable that the aluminosilicate introduced into the hydrosol have a weight mean particle diameter of less than about 40 microns and preferable less than 15 microns, and when large particles are desired between 2 and 7 microns. The use of aluminosilicate having a weight mean particle diameter in excess of 40 microns gave rise to a physically weak product while the use of aluminosilicate having a weight mean particle diameter of less than 1 micron produced a product of low diffusivity.

The powder-containing inorganic oxide hydrosol sets to a hydrogel after lapse of a suitable period of time and the resulting hydrogel is base exchanged, if zeolite alkali metal has been introduced as a result of employing an alkali metal aluminosilicate, with a solution containing at least one ion selected from the group consisting of alkaline earth metals, rare earth metals, ammonium and hydrogen. The base exchanged product is thereafter dried to a gel and thermally activated at a temperature below the fusion point of the incorporated aluminosilicate powder.

The inorganic oxide gel employed as a matrix for the aluminosilicate powder may be a gel of any hydrous inorganic oxide, for example, aluminous or siliceous gels. While alumina gel or silica gel may be utilized as a suitable matrix, it is preferred that the inorganic oxide gel employed be a cogel of silica and an oxide of at least one metal selected from the group consisting of metals of Groups IIA, IIIB, and IVA of the Periodic Table. Such components include, for example, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania, as well as ternary combinations such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina - magnesia and silica - magnesia-zirconia. Particular preference is accorded cogels of silica-alumina, silica-zirconia and silica-alumina-zirconia. In the foregoing gels,

silica is generally present as the major component and the other oxides of metals are present in minor proportion. Thus, the silica content of such gels is generally within the approximate range of 55—100 weight per cent with the metal oxide content ranging from 0—45 weight per cent. The inorganic oxide hydrosols utilized herein and hydrogels obtained therefrom may be prepared by any method well known in the art such as, for example, hydrolysis of ethyl ortho silicate, acidification of an alkali metal silicate which may contain a compound of a metal, the oxide of which it is desired to cogel with silica. The relative proportions of finely divided aluminosilicate and matrix may vary widely with the aluminosilicate content ranging from about 2 to about 90% by weight and more usually, particularly where the composite is prepared in the form of beads, in the range of about 2 to about 50% by weight of the composite. Other preferred matrices include clays and hydrous alumina prepared by any well known techniques.

The aluminosilicate combined with an inorganic oxide gel may suitably be prepared by initially forming a hydrosol-containing added aluminosilicate powder, permitting the same to set in mass to a hydrogel which is thereafter dried and broken into pieces of desired size. The pieces of gel so obtained are generally of irregular shape. Uniformly shaped pieces of gel may be obtained by extrusion or pelleting of the aluminosilicate containing hydrogel. Also, the hydrosol may be introduced into the perforations of a perforated plate and retained therein until the sol has set to a hydrogel, after which the formed hydrogel pieces are removed from the plate. The method of the invention is particularly useful for the production of catalyst in the form of spheroidal particles. The hydrosol-containing powder aluminosilicate may be made into spheroidal particles in manners known per se.

While for the production of spheroidal catalyst particles, initial formation of a hydrosol which sets upon lapse of a short interval of time to an all-embracing bead-form hydrogel is essential, it is within the purview of this invention to also employ particularly where the catalyst is prepared in a form other than the spheroidal shape, a matrix comprising a gelatinous hydrous oxide precipitate with varying degrees of hydration or a mixture of a hydrogel and such gelatinous precipitate. The term gel as utilized herein is intended to include hydrogel, gelatinous precipitates and mixtures of the two. Also, the matrix may consist of or contain as a component thereof a clay and particularly a clay of the montmorillonite or kaolinite families, either raw or acid treated. Other suitable materials for use as the matrix of the present catalyst composition include charcoal, graphite, bauxite, metallic powder, and other binders compatible with the aluminosilicate and thermally stable under the temperature conditions at which the catalyst is used.

The alkali metal aluminosilicate prepared by the specified treatment of natural clay may undergo base exchange either before or after intimate admixture thereof with the binder therefor. Base exchange is effected by treatment with a solution containing alkaline earth metal ions, rare earth metal ions, ammonium ions, hydrogen ions or mixtures of one with the other. It is contemplated that any compound capable of ionization to yield one or more of the aforementioned ions may be employed for base exchange. Generally, an aqueous solution of an alkaline earth metal salt, a rare earth metal salt, an acid or an ammonium salt will be employed. Thus, the alkaline earth metal salt may be a chloride, nitrate, formate or acetate of calcium or magnesium. The rare earth metal salt employed may be a chloride, sulfate, nitrate formate or acetate of cerium, lanthanum, praseodymium, neodymium, samarium and other rare earths as well as solutions containing mixtures of these ions and mixtures of the same with other ions such as ammonium. Weak acid solutions or treatment of the aluminosilicate with an acidic gas serves to effect exchange of the alkali metal with hydrogen ions. Base exchange of the aluminosilicate may also be readily effected with solutions containing ammonium ions to yield ammonium aluminosilicates which, upon heating, result in the hydrogen form of the aluminosilicate. Another effective method of exchange is to replace more than about 70 per cent of the alkali metal ion by contact with a solution of an alkaline earth metal ions, rare earth metal ions or rare earth metal and ammonium ions, followed by completing the alkali metal exchange to less than about 3 per cent, preferably less than about 2 per cent, residual exchangeable alkali metal content with ammonium ion exchange.

The exchangeable alkali metal content of the finished catalyst should preferably be less than about 3 and preferably less than about 2 per cent by weight. The base exchange fluid may be contacted with the aluminosilicate in the form of a fine powder, a compressed pellet, extruded pellet, spheroidal bead or other suitable particle shape. It has been found that the desired base exchange may be effected most readily if the alkali metal aluminosilicate undergoing treatment has not previously been subjected to a temperature above about 600°F.

While water will ordinarily be the solvent in the base exchange solutions employed, it is contemplated that other solvents, although generally less preferred, may be used. Thus, in addition to aqueous solution, alcoholic solutions of suitable compounds as noted

above may be employed in producing the catalyst utilized in the present process. It will be understood that compounds employed for the base exchange solution undergo ionization in the particular solvent used.

The concentration of compound employed in the base exchange solution may vary depending on the nature of the particular compound used, on the alkali metal aluminosilicate undergoing treatment and on the conditions under which treatment is effected. Generally, the concentration of compound, the cation of which replaces alkali metal from the alkali metal aluminosilicate, is within the range of 0.2 to 30% by weight, although, as noted hereinabove, other solution concentrations may be employed providing the exchangeable alkali metal content is preferably reduced to less than about 3, preferably less than 2% by weight, and still more desirably to below 1% by weight.

The temperature at which base exchange is effected may vary widely, generally ranging from room temperature to an elevated temperature below the boiling point of the treating solution. While the volume of base exchange solution employed may vary widely, generally an excess is employed and such excess is removed from contact with the aluminosilicate after a suitable period of contact. The time of contact between the base exchange solution and aluminosilicate may vary widely depending on the temperature of the solution, the nature of the alkali metal aluminosilicate used and the particular compound employed for base exchange. Thus, the time of contact may extend from a brief period of the order of a few minutes for small particles to longer periods of the order of days for large pellets.

After base exchange treatment, the product is removed from the treating solution. Anions introduced as a result of treating with the base exchange solution may, if desired or necessary, be removed by water washing the dried composite for such period of time until the same is free of said anions. The washed product is then dried, generally in air to remove substantially all of the water therefrom. While drying may be affected at ambient temperature, it is more satisfactory to facilitate the removal of moisture by maintaining the product at a temperature between about 150 and about 600°F. for 4 to 48 hours.

The dried material is then subjected to calcination by heating in an inert atmosphere, i.e. one which does not adversely effect the catalyst such as air, steam, nitrogen, hydrogen, flue gas, helium or other inert gas. Generally, the dried material is heated in air to a temperature in the approximate range of 500°F. to 1500°F. for a period of at least about one hour and usually between about 1 and 48 hours. The catalyst is also improved by treating with steam either in place of or subsequent to the calcination step. Such steam treatment is feasibly carried out at temperatures between about 800 and 1500°F. at steam concentrations greater than about 5% for a time sufficient to reduce the catalyst surface area by at least 20% but not more than about 75%.

Cracking, utilizing the catalyst described herein, may be carried out at catalytic cracking conditions employing a temperature within the approximate range of 500 to 1200°F. and under a pressure ranging from subatmospheric pressure up to several hundred atmospheres. The contact time of the hydrocarbon charge within the catalyst is adjusted in any case according to the conditions, the particular oil feed and the particular results desired to give a substantial amount of cracking to lower boiling products. Cracking may be effected in the presence of the instant catalyst utilizing well-known techniques including, for example, those wherein the catalyst is employed as a fluidized mass or as a compact particle-form moving bed.

The cracking activity of the catalyst is a measure of its capacity to catalyze conversion of hydrocarbons and is expressed herein as the percentage conversion of a Mid-Continent Gas Oil having a boiling range of 450 to 950°F. to gasoline having an end boiling point of 410°F. by passing vapors of said gas oil through the catalyst at 875°F. to 900°F., substantially atmospheric pressure and a feed rate of 1.5 to 8 volumes of liquid oil per volume of catalyst per hour for 10 minute runs between regenerations.

It has been found desirable in analyzing the results obtained with the catalyst described herein to compare the same with those realized with a conventional commercial silica-alumina gel cracking catalyst containing approximately 10% by weight alumina. The exceptional activity and selectivity of the present catalyst are emphasized by comparison of the various product yields obtained with such catalyst with yields of the same products given by the conventional silica-alumina catalyst at the same conversion level. The differences ($\Delta$ values) shown hereinafter represent the yields given by the present catalyst minus the yields given by the conventional catalyst.

The following examples will serve to illustrate the catalyst and method of the present invention without limiting the same:

EXAMPLE 40

Dixie clay used in this preparation is a kaolinite having the following composition: 44.51 wt.% $Al_2O_3$, 38.51 wt. % $SiO_2$, 1.27 wt.% $Fe_2O_3$, 1.47 wt.% $TiO_2$, 0.08 wt.% CaO, 0.12 wt.% MgO, 0.08 wt.% $Na_2O$ and 0.22 wt.% $K_2O$.

One thousand (1000) grams of the above clay were mixed in a blendor with 2600 grams NaOH pellets containing 77.5 wt.% $Na_2O$,

1000 grams of water and 1840 grams N-Brand sodium silicate containing 8.8 wt.% $Na_2O$, 28.5 wt.% $SiO_2$ and 62.7 wt.% $H_2O$. The resulting wet slurry was placed in a furnace at 600°F. and held for 4 hours permitting the temperature of the slurry to increase from room temperature to 600°F.

The product which formed was a hard crusty solid. This material was ball-milled to a particle size of less than about 60 mesh (Tyler). The ground material was then contacted with 6500 cc of water and ball milled for an additional 4 hours. The resulting slurry was divided into three equal parts and diluted with an additional 7707 cc of water each.

This slurry was digested in a water bath at 200°F. for 20 to 24 hours. After digestion, the supernatant liquid was separated from the resulting activated clay by filtration and the filter cake combined from the three diluted portions was washed free of water-soluble matter.

The activated clay, as wet cake contained 42.2 weight per cent solids (as determined by drying a sample at 230°F). Cyclohexane adsorption capacity of the dried sample amounted to 5.7 weight per cent. By X-ray analysis, the clay was shown to be mainly amorphous possessing only a small amount of crystalline character.

The activated clay, so obtained, was incorporated into a silica-alumina hydrogel matrix in bead form as follows:

A. Silicate Solution
  1. 15.75 lbs. N-Brand sodium silicate
     7.95 lbs. Water
  2. Clay Slurry
     4.05 lbs. activated clay slurry
     5.62 lbs. water

The above two solutions were mixed together forming the slurry-silicate solution having a specific gravity at 76°F. of 1.195.

B. Acid Solution
    57.10 lbs. Water
    4.23 lbs. $Al_2(SO_4)_3.18H_2O$
    1.98 lbs. $H_2SO_4$ (97.6%)
    Specific Gravity at 80°F. of 1.051

Solutions A and B were mixed together in a mixing nozzle at a rate of 390cc/min. for Solution A and 386 cc/min. for Solution B to yield a hydrosol having a pH of 8.1 to 8.6 The resulting hydrosol was introduced in the form of globules into a body of water-immiscible liquid in which they set to beads of hydrogel in 2.8 seconds at a temperature 64°F. The composition of the resulting hydrogel beads, on a calcined salt-free basis, was 25.3 weight per cent activated clay, 4.6 weight per cent alumina and remainder silica.

The bead hydrogel, so obtained, was base exchanged with a 2 per cent by weight aqueous solution of a mixture of rare earth metal chlorides, continuously for 24 hours using the equivalent of 12 (2 hour) changes with 1/2 volume of solution per volume of beads. The approximate composition of the rare earth metal chloride mixture utilized for base exchange was:

|  | Weight Per Cent |  |
|---|---|---|
| $LaCl_3.6H_2O$ — | 23 |  |
| $CeCl_3.6H_2O$ — | 43.5 | 70 |
| $PrCl_3.6H_2O$ — | 5.4 |  |
| $NdCl_3.6H_2O$ — | 17.9 |  |
| $SmCl_3.6H_2O$ — | 1.9 |  |
| $GdCl_3.6H_2O$ — | 0.6 |  |
| Other rare earth chloride |  | 75 |
| hexahydrates | 0.2 |  |

Plus small amounts of salts of Th, Ca, Mg, Na and Al, as well as some silica.

The base exchanged bead hydrogel was then water washed free of soluble chlorides, dried in air at 270°F. for 24 hours, tempered 10 hours at 1000°F. in air and finally stabilized in two ways, i.e. by treatment with steam for 20 hours at 1225°F. at atmospheric pressure and by treating with steam for 30 hours at 1200°F. and a pressure of 15 psig.

The finished catalyst had a sodium content of 0.66 weight per cent, a rare earth metal oxide content of 16 weight per cent and had a surface area after the 20 hours steam treat at 1225°F. with steam at atmospheric pressure of 208 square meters per gram.

EXAMPLE 41

The catalyst of this example was prepared in a manner identical with that of Example 40 except that instead of base exchanging the bead hydrogel obtained with a 2 weight per cent solution of rare earth metal chlorides, base exchange was carried out with a combined solution containing 1 weight per cent rare earth metal chloride and 1 weight per cent ammonium chloride. The base exchanged material was thereafter washed, dried, tempered and steam treated as in Example 40.

The finished catalyst of this example had a sodium content of 0.56 weight per cent a rare earth metal oxide content of 8.2 weight per cent and possessed a surface area after the 30 hour steam treat at 1200°F. with steam at 15 psig of 104 square meters per gram.

Catalytic evaluation of the catalysts of Examples 40 and 41 is hereinafter summarized in Table IV. Referring more particularly to such table, it will be seen that these catalysts containing the caustic-silicate activated clay, even though mainly in an amorphous condition, are more active than catalysts of Example A which was a standard silica-alumina cracking catalyst or Example B which was a catalyst similar to that of Example A but base exchanged with the rare earth metal chloride mixture. The activity advantage was about +5 volume per cent conversion at 4 liquid hourly space velocity for the catalyst of Example 40 and about +8 volume per cent conversion for the catalyst of Example 41. Both of these catalysts were more selective, affording a +4.9 and a +2.6

volume per cent $C_5+$ gasoline advantage over the standard silica-alumina catalyst. More severe steam treat of 30 hours at 1200°F. and 15 psig decreased the selectivity advantage with the catalyst of Example 40 and increased the selectivity advantage with the catalyst of Example 41 to +3.5 $C_5+$ gasoline advantage over standard silica-alumina catalyst.

EXAMPLE 42

The catalyst of this example was prepared in the same manner as that of Example 40 except that the Dixie clay was activated to a greater degree, yielding activated clay which had a cyclohexane adsorption of 10 weight per cent corresponding to a crystallinity of about 42 per cent.

The Dixie clay was activated as follows: For each of eight batches of 125 grams of Dixie clay, 187.5 grams NaOH containing 77.5% $Na_2O$, 125 grams of water and 230 grams N-Brand sodium silicate containing 28.5 wt.% $SiO_2$, 8.8 wt.% $Na_2O$ and 62.7 wt.% $H_2O$ were mixed with vigorous agitation. Batches of the slurry were placed in a furnace at 600°F. and held for 4 hours permitting the temperature of the slurry to increase from room temperature to 600°F. The fused material so obtained was blended with 1500 cc of water for approximately 2 minutes and then diluted to 8000 cc with water and digested for 68 hours at 200°F. The activated clay slurry was filtered and water washed free of soluble matter. The total yield of wet cake from the eight batches was 5.14 pounds having a solids content of 60.25 per cent (as determined by drying a sample at a temperature of 230°F.)

The activated clay, prepared as above, was used in the preparation of the present catalyst in a manner identical with that of Example 40 by introducing in a silica-alumina bead hydrogel matrix, base exchanging with rare earth chloride solution, washing, drying, calcining and treating with 100 per cent steam at 15 psig and 1200°F. for 30 hours.

The finished catalyst of this example had a sodium content of 0.52 weight per cent, a rare earth metal oxide content of 14.7 weight per cent, an alumina content of 12.7 weight per cent and a surface area of 161 square meters per gram after the pressure steam treat at 1200°F.

EXAMPLE 43

Utilizing the Dixie clay activated as in Example 42, the catalyst of this example was prepared in the same manner as that of Example 41 by introducing the activated clay into a silica-alumina bead hydrogel matrix, base exchanging with combined rare earth metal chloride and ammonium chloride solution, washing, drying, calcining and treating with 100 per cent steam at 15 psig and 1200°F. for 30 hours.

The finished catalyst of this example had a sodium content of 0.13 weight per cent, a rare earth metal oxide content of 11.5 weight per cent and a surface area of 147 square meters per gram after the pressure steam treat.

Catalytic evaluation of the catalysts of Examples 42 and 43 using a clay activated to a higher degree with a cyclohexane adsorption of 10 weight per cent, exhibited more active and selective cracking than the catalysts of Examples 40 and 41 as will be seen from the data summarized hereinafter in Table IV. Thus, the catalyst of Example 43 gave 59.2 volume per cent conversion at 4 liquid hourly space velocity compared to 38 volume per cent conversion using the catalyst of Example 41. The catalyst of Example 43, it will further be noted, was also very selective affording +6.3 volume per cent $C_5+$ gasoline, −1.9 weight per cent dry gas and −1.5 weight per cent coke in comparison with the standard silica-alumina catalyst. The catalyst of Example 42 affording a 49 volume per cent conversion at 4 liquid hourly space velocity was substantially more active than the catalyst of Example 40. The selectivity of the catalyst of Example 42 was also good showing +3.8 volume per cent $C_5+$ gasoline yield, −0.6 weight per cent dry gas and −0.4 weight per cent coke advantage over the standard silica-alumina catalyst. Comparing the catalyst of Example 43 with that of Example 42, the particular advantage of the combined rare earth metal chloride and ammonium chloride base exchange is evident in both activity and selectivity.

Table IV summarizing the foregoing is set forth below:

## Table IV

| Example | A | A | B | 40 | 40 | 40 | 41 | 41 | 41 | 42 | 43 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Description Matrix | $SiO_2$ — $Al_2O_3$ — — — — → $SiO_2$ — $Al_2O_3$ + Dixie Clay Caustic Activated — — — — — — — → | | | | | | | | | | |
| Base Exchange Solution | $Al_2(SO_4)_3$.18$H_2O$ | | $RECl_3$.6$H_2O$ | $RECl_3$.6$H_2O$ | | | $RECl_3$ + $NH_4Cl$ | | | $RECl_3$.6$H_2O$ | $RECl_3$+$NH_4Cl$ |
| Conc., wt. % | 1.5 | | | 2 | | | 1 | 1 | | 2 | 1  1 |
| Composition | | | | | | | | | | | |
| Na, wt. % | 0.19 | | 0.61 | 0.66 | | | 0.56 | | | 0.52 | 0.13 |
| (RE)$_2$O$_3$, wt. % | | | 6.19 | 16.0 | | | 8.2 | | | 14.7 | 11.5 |
| Al$_2$O$_3$, wt. % | 9.37 | | | | | | | | | 12.7 | |
| Steamtreat (1) | SR | SR | SR | SR | SR | SP | SR | SP | SP | SP | SP |
| Physical Properties | | | | | | | | | | | |
| App. Dens. g/cc. | | | | | | | | | | 0.70 | 0.66 |
| Surface Area (after steaming) m²/g. | 206 | | 225 | 208 | | | 104 | | | 161 | 147 |
| Catalytic Evaluation | | | | | | | | | | | |
| Conversion, vol. % | 37.9 | 50.1 | 34.2 | 43.9 | 43.2 | 33.3 | 46.3 | 38.0 | 47.6 | 49.0 | 59.2 |
| LHSV (3) | 4 | 2 | 4 | 2 | 4 | 4 | 4 | 4 | 2 | 4 | 4 |
| 10 RVP (4) Gaso., vol. % | 32.7 | 36.9 | | 36.1 | 41.3 | 31.5 | 40.0 | 36.2 | 41.0 | 43.0 | 51.0 |
| Excess C₄'s vol. % | 7.4 | 14.8 | | 7.1 | 3.6 | 3.6 | 7.4 | 4.7 | 7.8 | 7.1 | 10.1 |
| C₅ + Gasoline, vol. % | 31.1 | 35.9 | 27.0 | 34.1 | 38.2 | 29.4 | 37.7 | 33.9 | 38.7 | 40.7 | 48.5 |
| Total C₄'s, vol. % | 9.1 | 15.8 | | 9.1 | 6.7 | 5.8 | 9.6 | 7.0 | 10.1 | 9.5 | 12.7 |
| Dry gas, wt. % | 4.3 | 7.0 | | 5.7 | 3.9 | 3.2 | 4.7 | 3.5 | 5.0 | 5.4 | 5.6 |
| Coke, wt. % | 1.0 | 2.3 | | 2.3 | 2.0 | 1.3 | 2.6 | 0.5 | 2.2 | 2.2 | 2.9 |
| H₂, wt. % | | | | 0.19 | 0.19 | 0.17 | 0.22 | 0.11 | 0.18 | 0.18 | 0.11 |
| Δ Values to standard silica-alumina catalyst (2) | | | | | | | | | | | |
| 10 RVP, vol. % | | | | 0.0 | +5.6 | +1.5 | +2.5 | +3.5 | +2.7 | +4.0 | +6.5 |
| Excess C₄'s vol. % | | | | −1.6 | −4.6 | −2.6 | −2.2 | −2.6 | −2.0 | −3.2 | −3.4 |
| C₅ + Gasoline, vol. % | | | | +0.4 | +4.9 | +1.4 | +2.6 | +3.5 | +2.7 | +3.8 | +6.3 |
| Total C₄'s, vol. % | | | | −2.0 | −4.3 | −2.7 | −2.2 | −2.6 | −2.2 | −3.1 | −3.0 |
| Dry Gas, wt. % | | | | +0.7 | −0.9 | −0.4 | −0.7 | −0.7 | −0.6 | −0.6 | −1.9 |
| Coke, Wt. % | | | | +0.2 | +0.02 | −0.1 | +0.2 | −1.1 | −0.5 | −0.4 | −1.5 |

(1) SR — 20 hours at 1225° F. with 100% Atmos. steam SP — 15 psig steam treat at 1200° F. for 30 hours.
(2) Commercial silica-alumina gel cracking catalyst containing about 10 wt. % $Al_2O_3$ and remainder $SiO_2$.
(3) Liquid Hourly Space Velocity, defined as the volumes of feed which contact unit volume of catalyst after reduction to 60° F.
(4) Reid Vapour Pressure, defined as a vapour pressure of a hydrocarbon at 100° F

The following Examples 44 and 45 demonstrate the particular high catalytic activity and selectivity possible with the undiluted clay activated to a varying degree of crystallinity and thereafter base exchanged with rare earth metals and ammonium chloride solutions forming rare earth acid aluminosilicates.

EXAMPLE 44

Dixie clay was activated as described in Example 40 to yield a product having a cyclohexamine adsorption capacity of 5.7 wt.%. The clay was shown by X-ray analysis to be mainly amorphous.

The activated clay was base exchanged continuously for 48 hours at 180°F. with an aqueous solution containing 5% by wt. of the rare earth metal chloride mixture described in Example 40 and 2% by wt. of ammonium chloride. Such continuous base exchange is equivalent to 24 (2 hour) changes with 1/2 volume of solution per volume of slurry. The base exchanged clay was thereafter water washed free of chloride ion, air dried at 270°F. for 24 hours, tempered 10 hours at 1000°F. in air and then stabilized by steam treating first at 1225°F. for 20 hours and atmospheric pressure, followed by a 30 hour steam treat at 1200°F. at a pressure of 15 psig.

The finished catalyst had a sodium content of 0.30 wt.%, and a rare earth metal oxide content of 27.2 wt.%.

Catalytic evaluation data hereinafter set forth in Table V show that marked advantages over standard silica-alumina cracking catalysts are realized by activating the clay by caustic-silicate fusion and subsequently base exchanging with a rare earth metal-ammonium chloride solution. Thus, the catalyst of Example 44 afforded a 40 volume per cent conversion as a liquid hourly space velocity of 10 and a conversion of 47 volume per cent at a liquid hourly space velocity of 4. In addition, this catalyst showed selectivity advantages of +4.1 and +3.2 volume per cent $C_5$+ gasoline over standard silica-alumina cracking catalyst at the same conversions. The standard silica-alumina catalyst (Example A) at a liquid hourly space velocity of 4 provided only 37.9 volume per cent conversion of the charge stock.

EXAMPLE 45

The catalyst of this example was prepared in the same manner as that of Example 44 except that the Dixie clay was activated as described in Example 42 to a greater degree having a cyclohexane adsorption of 10 wt.% and a crystallinity of about 42%.

The activated clay was base exchanged, washed, dried, tempered and steam treated for 30 hours at a temperature of 1200°F. and a pressure of 15 psig.

The finished catalyst had a sodium content of 0.27 wt.%, a rare earth metal oxide content of 24. wt.% and had a surface area after the steam treatment of 221 square meters per gram.

Catalytic evaluation data obtained with this catalyst are hereinafter set forth in Table V. These data show that a high catalytic activity and selectivity were realized with this rare earth metal-ammonium chloride exchanged activated clay. Thus, this catalyst afforded 55.4 volume per cent conversion at a liquid hourly space velocity of 16. At this high liquid hourly space velocity the catalyst also showed +7.8 volume per cent $C_5$+ gasoline advantage over the standard silica-alumina cracking catalyst. The improvement noted with the catalyst of this example over that of Example 44 would appear to be attributable to the increase in crystallinity of the activated clay employed.

Table V summarizing the foregoing is set forth below:

TABLE V

| Example | 44 | | 45 |
|---|---|---|---|
| Description | Activated Clay | | Activated Clay |
| **Base Exchange** | | | |
| Solution | RECl$_3$ + NH$_4$Cl — — — — — — — — → | | |
| Conc. wt. % | 5 | 2 — — — — — — — → | |
| **Composition** | | | |
| Na, wt. % | 0.30 | | 0.27 |
| (RE)$_2$O$_3$, wt. % | 27.2 | | 24.0 |
| Steamtreat (1,2) | SR20 | SP30 | SP30 |
| **Physical Properties** | | | |
| App. Dens. g/cc. | | | |
| Surface Area (after steaming) m$^2$/g. | | | 221 |
| **Catalytic Evaluation** | | | |
| Conversion, vol. % | 40.3 | 47.2 | 55.4 |
| LHSV | 10 | 4 | 16 |
| 10 RVP Gaso., vol. % | 38.4 | 41.2 | 50.9 |
| Excess C$_4$'s, vol. % | 4.8 | 7.4 | 7.8 |
| C$_5$ + Gasoline, vol. % | 35.9 | 38.8 | 48.2 |
| Total C$_4$'s, vol. % | 7.3 | 9.8 | 10.6 |
| Dry Gas, wt. % | 3.5 | 5.3 | 4.8 |
| Coke, wt. % | 1.0 | 1.8 | 1.7 |
| H$_2$, wt. % | 0.03 | 0.14 | 0.05 |
| **Δ Values to standard silica-alumina catalysts (4)** | | | |
| 10 RVP, vol. % | +4.4 | +3.1 | +8.4 |
| Excess C$_4$'s, vol. % | −3.1 | −2.3 | −4.5 |
| C$_5$ + Gasoline, vol. % | +4.1 | +3.2 | +7.8 |
| Total C$_4$'s, vol. % | −2.9 | −2.2 | −4.0 |
| Dry Gas, wt. % | −1.0 | −0.2 | −2.0 |
| Coke, wt. % | −0.7 | −0.7 | −2.1 |

(1) SR20 steamtreat 20 hours at 1225° F. atmospheric steam.

(2) SP30 steamtreat 30 hours at 15 psig.

(4) Commerical silica-alumina gel cracking catalyst containing about 10 wt. % Al$_2$O$_3$ and remainder SiO$_2$.

As indicated hereinabove, the degree of clay conversion can be controlled by adjustment in the ratios of total alkali metal oxide/water-free clay, silica-water-free clay and water/total alkali metal oxide during the initial high temperature step and the subsequent digestion step. Products ranging from amorphous to highly crystalline alkali metal aluminosilicates may be prepared depending upon the above indicated variables. Numerical limits on the above ratios have been specified hereinabove to afford amorphous or products of low crystallinity to those characterized by a high crystallinity. The relationship between total alkali metal oxide, water-free clay and added silica in the reaction mixture is more particularly shown by the accompanying Figure 4.
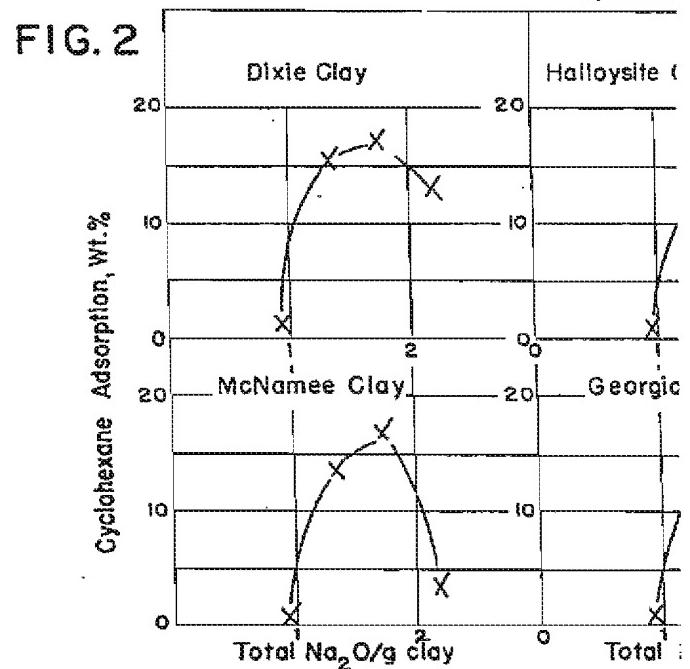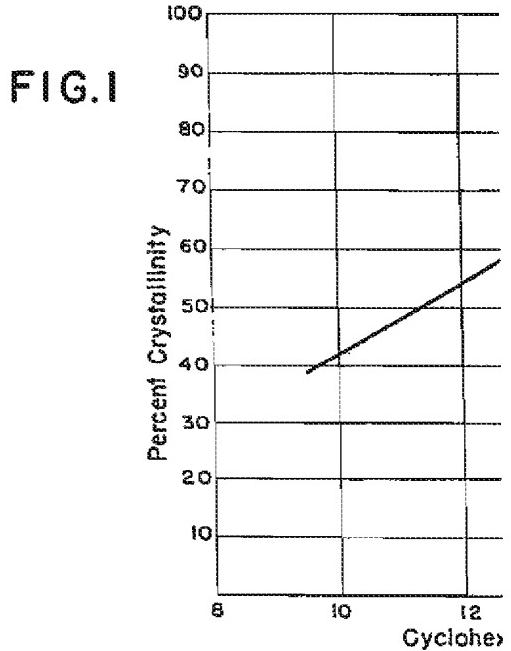
To obtain products of a highly crystalline nature, it has been established that the proportions of the reactants are such that the composition of the reaction mixture falls within the area ABCD of Figure 4.
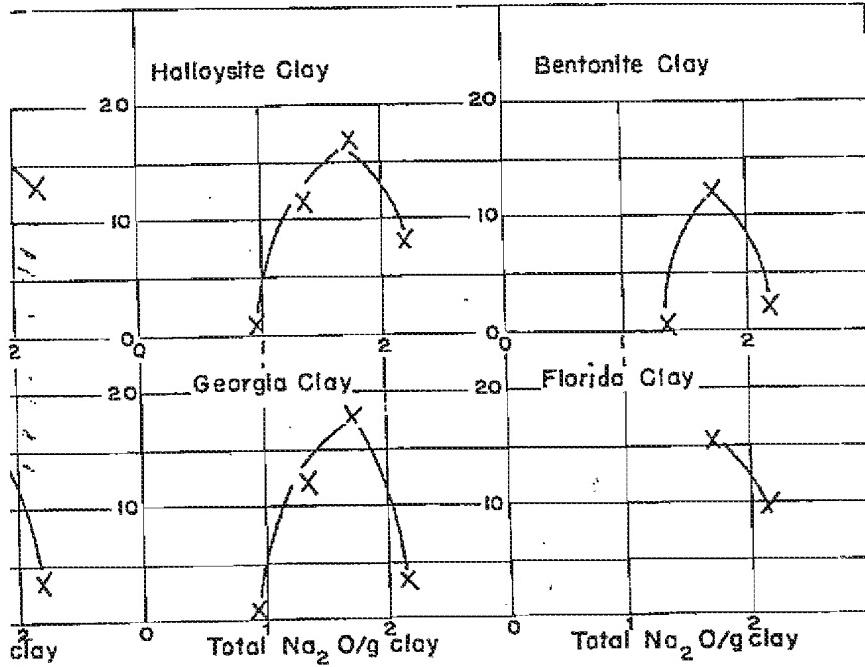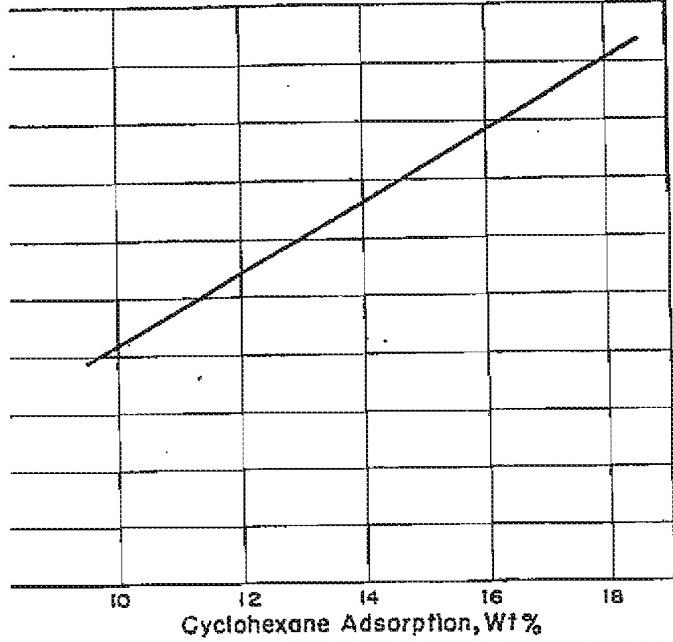
WHAT WE CLAIM IS:—

1. A method for preparing a crystalline aluminosilicate zeolite having the crystal structure common to zeolites X and Y which comprises forming a frit from an aqueous slurry of clay, alkali metal hydroxide and either silica or a precursor thereof by maintaining the slurry at a temperature between about 230°F and about 1600°F, the composition of the slurry falling within the following limits:

Weight Ratio of Total Alkali Metal Oxide/
Water-Free Clay = 0.95 to 7.4
Weight Ratio of Silica/Water-Free Clay = .01
to 3.8,
5 and digesting the frit in water at a tempera-
ture in the approximate range of 180°F to
220°F until crystalline aluminosilicate forms,
the mole ratio of water to total alkali metal
oxide of the frit being within the approximate
10 range of 35 to 180.

2. A method according to claim 1, wherein
formation of the frit is completed after the
slurry has been maintained at said tempera-
ture for a period of from 3 minutes to 72
15 hours.

3. A method according to claim 1 or 2,
wherein the Weight Ratio of Total Alkali
Metal Oxide/Water-Free Clay = 1.1 to 6.6.

4. A method according to claim 3, wherein
20 the Weight Ratio of Total Alkali Metal
Oxide/Water-Free Clay = 1.1 to 5.1, Weight
Ratio of Silica-Water-Free Clay = 0.19 to 3.3
and the mole ratio of water to total alkali
metal oxide is within the approximate range
25 of 35 to 115.

5. A method according to any of claims 1
to 4, wherein the clay is raw uncalcined
natural clay.

6. A method according to any of the pre-
30 ceding claims, wherein before said digestion
the frit is ground to less than 60-mesh particle
size and dispersed in water in the proportion
of 3 parts solid to 1 part of water.

7. A method according to any of the pre-
35 ceding claims, wherein the composition of
the slurry falls within the area ABCD, prefer-
ably within the area EFGH of accompany-
ing Figure 4.

8. A method according to claim 7, wherein
40 the composition of the slurry falls within the
area EFGH of accompanying Figure 4.

9. A method according to any of the pre-
ceding claims, wherein the silica is present in
the form of alkali metal silicate, sand or
45 colloidal suspension of silica.

10. A method according to any of the pre-
ceding claims, wherein the alkali metal
hydroxide is sodium hydroxide.

11. A method according to any of the pre-
50 ceding claims, wherein the resultant slurry of
crystalline aluminosilicate is spray-dried to
yield a product in finely divided form.

12. A method according to any of the pre-
ceding claims, wherein the alkali metal crys-
55 talline aluminosilicate formed is base-
exchanged with a solution containing at least
one monovalent or divalent ion selected from

alkaline earth metals, rare earth metals,
ammonium, hydrogen, silver, magnesium and
transition metals. 60

13. A method according to claim 12,
wherein the resulting base - exchanged
aluminosilicate is intimately mixed, in finely
divided form, with a binder therefor, the
resulting composite being dried and calcined. 65

14. A method according to claim 13,
wherein the binder is a clay or an inorganic
oxide gel.

15. A method according to claim 13 or 14,
wherein the binder is an inorganic oxide sol 70
gelation of which is effected after the intimate
mixing, the resulting composite being washed
free of soluble matter before the drying and
calcining.

16. A modification of the method claimed 75
in claim 15, wherein the aluminosilicate is
base-exchanged after formation of said com-
posite.

17. A method according to claim 15 or 16,
wherein the hydrosol is a siliceous hydrosol, 80
and the aluminosilicate constitutes between
about 2 and about 90 per cent by weight of
the dried composite.

18. A method according to claim 17, where-
in the sol is in the form of spheroidal particles 85
when gelation is effected.

19. A method according to any of claims
12 to 18, wherein the base-exchange decreases
the exchangeable alkali metal content of the
aluminosilicate to less than 3 per cent by 90
weight on a dry solids basis.

20. A method of making a crystalline
aluminosilicate substantially as herein des-
cribed with reference to any of Examples
1—4, 7—16 and 20—39. 95

21. A method of making a crystalline
aluminosilicate catalytic composition substan-
tially as described in any of Examples 40 to
45.

22. A crystalline aluminosilicate or com- 100
position containing same whenever prepared
by the method of any of the preceding claims.

23. A process for converting hydrocarbons,
particulary cracking the same, which com-
prises contacting a hydrocarbon charge with 105
aluminosilicate or aluminosilicate composition
as claimed in claim 22.

FIG.1



Percent Crystallinity

100
90
80
70
60
50
40
30
20
10

8    10    12

Cyclohe>

FIG. 2



Cyclohexane Adsorption, Wt.%

Dixie Clay                    Halloysite (

20                            20

10                            10

0                             0
                   2

McNamee Clay                 Georgic

20                            20

10                            10

0                             0
Total Na₂O/g clay            Total

Cyclohexane Adsorption, Wt%



Halloysite Clay

Bentonite Clay

Georgia Clay

Florida Clay

clay

Total Na$_2$O/g clay

Total Na$_2$O/g clay

FIG.1

Percent Crystallinity

Cyclohexane Adsorption, Wt %

FIG.2

Cyclohexane Adsorption, Wt.%

Dixie Clay

Halloysite Clay

Bentonite Clay

McNamee Clay

Georgia Clay

Florida Clay

Total Na₂O/g clay

Total Na₂O/g clay

Total Na₂O/g clay

50g.Raw Clay+75g.NaOH+92g. N-Brand Silicate

Mixture Fused 4Hrs.at 60C and Digested 21Hrs. at Dilution Indicated

Same as above using 26.2gram sand as source of Silica

Water-free Wt.%

## FIG. 3

v Clay+75g.NaOH+92g.
d Silicate

rture Fused 4Hrs.at 600°F
l Digested 21 Hrs. at
ution Indicated

s above using 26.2gram
i source of Silica

200      250      300

Na₂O

## FIG. 4

Total Alkali Metal Oxide
Wt. %

A
B
F
D
E
H
G
C

Water-free Clay
Wt. %

Added
SiO₂
Wt. %

FIG.3

⊙ 50g.Raw Clay+75g.NaOH+92g.
N-Brand Silicate

Mixture Fused 4Hrs.at 600°F
and Digested 21 Hrs.at
Dilution indicated

△ Same as above using 26.29gram
sand as source of Silica

Cyclohexane Adsorption, Wt.%

Mole Ratio H₂O/Na₂O



FIG.4

Total Alkali Metal Oxide
Wt.%

Water-free Clay
Wt.%

Added
SiO₂
Wt.%